

Contribution of motor vehicle emissions to organic carbon and fine particle mass in Pittsburgh, Pennsylvania: Effects of varying source profiles and seasonal trends in ambient marker concentrations

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Abstract

We present estimates of the vehicular contribution to ambient organic carbon (OC) and fine particle mass (PM) in Pittsburgh, PA using the chemical mass balance (CMB) model and a large dataset of ambient molecular marker concentrations. Source profiles for CMB analysis are selected using a method of comparing the ambient ratios of marker species with published profiles for gasoline and diesel vehicle emissions. The ambient wintertime data cluster on a hopanes/EC ratio–ratio plot, and therefore can be explained by a large number of different source profile combinations. In contrast, the widely varying summer ambient ratios can be explained by a more limited number of source profile combinations. We present results for a number of different CMB scenarios, all of which perform well on the different statistical tests used to establish the quality of a CMB solution. The results illustrate how CMB estimates depend critically on the marker-to-OC and marker-to-PM ratios of the source profiles. The vehicular contribution in the winter is bounded between 13% and 20% of the ambient OC (274 ± 56 – 416 ± 72 ng-C m⁻³). However, variability in the diesel profiles creates uncertainty in the gasoline–diesel split. On an OC basis, one set of scenarios suggests gasoline dominance, while a second set indicates a more even split. On a PM basis, all solutions indicate a diesel-dominated split. The summer CMB solutions do not present a consistent picture given the seasonal shift and wide variation in the ambient hopanes-to-EC ratios relative to the source profiles. If one set of source profiles is applied to the entire dataset, gasoline vehicles dominate vehicular OC in the winter but diesel dominates in the summer. The seasonal pattern in the ambient hopanes-to-EC ratios may be caused by photochemical decay of hopanes in the summer or by seasonal changes in vehicle emission profiles.

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1. Introduction

Gasoline and diesel motor vehicles are significant contributors to the ambient organic carbon (OC) and PM_{2.5} mass in urban environments (Schauer et al., 1996; Watson et al., 1998a; Fraser et al., 2003b). The chemical mass balance (CMB) model with individual organic compounds or molecular markers such as hopanes and polycyclic aromatic hydrocarbons (PAHs) is one way of quantifying the vehicular contribution to ambient OC, as well as the gasoline–diesel split.

Selection of source profiles and fitting species requires careful consideration when performing CMB analysis. More than 20 different source profiles with speciated organics data for gasoline and diesel vehicles have been published. The majority of these source profiles have been developed for use in California, Colorado, and Texas (Rogge et al., 1993; Watson et al., 1998a; Schauer et al., 1999; Fraser et al., 2002; Schauer et al., 2002). The appropriateness of applying these profiles to regions with different climates and vehicle fleets has not yet been established. Further, many parts of the United States are affected by regional transport of fine particulate matter; this transport mixes emissions from a large spatial domain which complicates the definition of the vehicular fleet and the selection of source profiles.

Each published source profile represents the emissions from a single or a small number of vehicles. A comparison of the published profiles reveals a wide range of emission rates and emission composition. This variability complicates selection of source profiles because the profiles used in CMB need to represent the aggregate emissions from the entire vehicle fleet. Co-linearity also limits the number of different vehicle profiles that can be simultaneously considered in the CMB model. For example, previous applications of CMB have either combined multiple source profiles to construct a fleet-average gasoline profile (Schauer et al., 1996; Zheng et al., 2002) or have used a single source profile to represent the gasoline vehicle fleet (Fraser et al., 2003b). The uncertainty estimates considered by CMB are typically based on analytical uncertainties used to develop the datasets without considering the effects of variability in source profiles on the solutions.

This paper has two goals. The first is to evaluate the suitability of published motor vehicle source profiles for use in CMB analysis of a large dataset of

ambient molecular concentrations collected in Pittsburgh, PA. The second is to examine the variability in CMB results due to source profile selection. The paper concludes with a discussion of the factors affecting the source contribution estimates, including vehicle fleet composition and seasonal variations in molecular marker concentrations. This paper is part of a series of papers examining source apportionment of primary organic aerosol in Pittsburgh, PA (Robinson et al., 2006b, c, d).

2. Methods

The EPA's CMB8 model (<http://www.epa.gov/scram001/>) was implemented to estimate the contribution of gasoline and diesel vehicle emissions and other primary sources to ambient OC in Pittsburgh, PA. The analysis uses ambient concentrations of individual organic compounds, PM_{2.5} organic and elemental carbon, and PM_{2.5} elemental composition measured on 96 days between 20 June 2001 and 1 July 2002. The data were collected as part of the Pittsburgh Air Quality Study (Wittig et al., 2004).

Samples for organic speciation were collected every day in July 2001 and for much of January 2002, and on a 1-in-6-day schedule during the rest of the study using a PM_{2.5} quartz/PUF sampler operating at 145 lpm. Prior to sampling, the quartz fiber filters were baked at 550 °C for a minimum of 4 h to remove any residual organics. The polyurethane foam (PUF) plugs were cleaned thoroughly with a mixture of solvents (dichloromethane, acetone, and hexane), dried in a clean vacuum dessicator, and stored in pre-cleaned glass jars shielded from light, till required for sampling. The relevant sampler parts and sample handling tools were solvent-rinsed before use. All solvents used were high-resolution GC/MS-grade or better. After sampling and prior to analysis, filter-PUF pairs were stored in pre-cleaned glass jars in a freezer (−18 °C or lower); samples were shipped overnight in coolers packed with dry ice for analysis at Florida International University. Prior to extraction, each sample was spiked with an internal standard consisting of a suite of seven perdeuterated *n*-alkanes (C12, C16, C20, C24, C28, C32 and C36). The samples were extracted using dichloromethane. The extracts from each filter-PUF pair were combined and the volume was reduced to about 1 ml by rotary evaporation; the volume was further reduced to about 250 µL using a gentle

stream of pure nitrogen prior to methylation using freshly prepared diazomethane. Methylation converts polar organic acids to their methyl ester analogs enabling their detection by gas chromatography–mass spectrometry (GC/MS). The methylated extracts were analyzed by GC/MS using electron impact ionization. Each analyte was quantified by reference to the internal standard, using a relative response factor determined with authentic standards. Organic and elemental carbon were measured on quartz filters analyzed by a thermal-optical transmission method based on the NIOSH-5040 protocol (Subramanian et al., 2004, 2006). Cellulose filter samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for PM_{2.5} elemental composition (Pekney and Davidson, 2005).

The selection of compounds included in the CMB model is a critical issue; all major sources of each compound must be included in the model and the species should be conserved during transport from source to receptor (Watson et al., 1998b). This paper uses the basic set of compounds and source classes developed by Schauer et al. (1996) and Schauer and Cass (2000). Our focus is the uncertainty associated with the use of different motor vehicle profiles on the CMB results.

The following species are included in the CMB model: iron, titanium, elemental carbon (EC), *n*-heptacosane, *n*-nonacosane, *n*-hentriacontane and *n*-tritriacontane; iso-hentriacontane, anteiso-dotriacontane; hexadecanoic (palmitic) acid, octadecanoic (stearic) acid, 9-hexadecenoic (palmitoleic) acid, cholesterol; syringaldehyde, sum of resin acids acetosyringone, levoglucosan; 17a(H),21b(H)-29-norhopane, 17a(H),21b(H)-hopane, 22R + S-17a(H), 21b(H)-30-homohopane, 22R + S,17a(H),21b(H)-30-bishomohopane; benzo[e]pyrene, indeno[1,2,3-cd]pyQJ;rene, benzo[g,h,i]perylene, and coronene. All of these species are included in every calculation. In certain scenarios we also include *n*-tetracosane and *n*-hexacosane in the CMB model. Uncertainties for individual compounds are the greater of the relative or absolute uncertainties. Absolute uncertainties are based on multiples of the minimum detection limits, while relative uncertainties were determined by analyzing multiple samples collected in parallel. Relative uncertainties range from $\pm 10\%$ to $\pm 30\%$, depending on the species. OC or PM is not included in the model as molecular markers for secondary organic aerosol and potentially other primary sources are not known.

Source profiles for eight source classes are included in the model: diesel vehicles, gasoline vehicles, road dust, biomass combustion, cooking emissions, coke production, vegetative detritus, and cigarette smoke. Source profiles for cooking emissions and biomass smoke are taken from the literature, while a coke-oven emissions profile and Pittsburgh-specific vegetative detritus and road-dust profiles were developed as part of PAQS. The complete list of source profiles used and their references are provided in the Supplementary Material (Table S1). In order to determine the contribution of each source profile to ambient OC, calculations are performed using source profiles normalized by the OC emission rates. The CMB estimates for motor vehicle emissions are not sensitive to the other source profiles included in the model. An exception is 7 October 2001—the day with the maximum biomass smoke OC and EC—when the motor vehicle estimates are sensitive to the specific biomass smoke profiles. A common set of non-motor vehicle source profiles is used in all simulations.

Source profiles for gasoline and diesel vehicles are selected based on comparisons with the ambient concentrations of different molecular markers using scatter and ratio–ratio plots, which allow a visual comparison of source profiles and ambient concentrations. Ratio–ratio plots are constructed using three species; one compound is selected as a reference to normalize the concentrations of the other two compounds (target species). The best reference compounds are relatively abundant, stable, and specific to the sources plotted. Source profiles appear as points on ratio–ratio plots and linear mixing lines can be drawn to visualize the effects of mixing of emissions from different sources. More details on the construction, interpretation, and mathematics of ratio–ratio plots are provided in Robinson et al. (2006a, b).

3. Results and discussion

3.1. Ambient concentrations of motor vehicle markers

The Pittsburgh dataset includes measurements of a number of compounds that are used as markers for motor vehicle emissions, including hopanes, steranes, polycyclic aromatic hydrocarbons (PAHs), and EC. Hopanes and steranes are associated with unburned lubricating oil and are emitted by both

gasoline and diesel vehicles (Zielinska et al., 2004). Certain PAHs are more prevalent in gasoline exhaust while diesel exhaust is relatively enriched in EC; therefore these species have been used to distinguish between emissions from these two source classes (Cadle et al., 1999b; Fraser et al., 2003a). However, PAH concentrations in Pittsburgh, PA are dominated by emissions from metallurgical coke production (Robinson et al., 2006b), diminishing their utility as vehicular markers.

Fig. 1 shows a time series of ambient concentrations of two of the hopanes: norhopane ($17\alpha(\text{H}),21\beta(\text{H})$ -29-norhopane) and hopane ($17\alpha(\text{H}),21\beta(\text{H})$ -hopane). The 24-h average concentrations of these compounds are usually less than 0.4 ng m^{-3} . Normalizing the hopanes by EC to account for differences in atmospheric dilution reveals that the hopanes are a factor of two to three higher in the winter than in the summer, as shown in Fig. 1c. The other hopanes and the steranes in the Pittsburgh dataset exhibit a similar seasonal pattern.

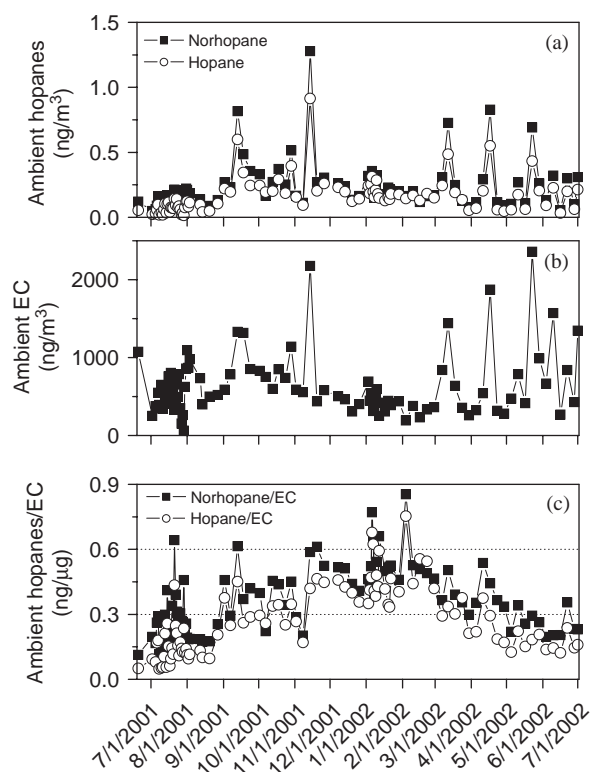


Fig. 1. Time series of ambient concentrations of (a) norhopane and hopane; (b) EC; and (c) the ratios of the two hopanes to EC. Panel (c) shows the strong seasonal variation in the ambient hopane concentrations relative to EC.

Ambient concentrations of the different hopanes are strongly correlated with linear-regression correlation coefficients greater than 0.95 as illustrated by the scatter plots in Fig. 2. From the perspective of CMB, these strong correlations mean that the ambient hopane data can be explained using a single-source profile (Robinson et al., 2006b)—presumably one that represents the aggregate emissions from motor vehicles.

Ambient 24-h average EC concentrations in Pittsburgh are generally between 0.5 and $1\text{ }\mu\text{g m}^{-3}$, with occasional large spikes (Fig. 1b). Fig. 2d shows that EC is modestly correlated ($R^2 = 0.65$) with norhopane (and by extension, with the other hopanes), but the R^2 value drops below 0.3 if the high concentration days (norhopane $> 0.4\text{ ng m}^{-3}$) are removed from the dataset. If the data are sorted by season, the R^2 values for the lower concentration days improve to about 0.6, though the summer and winter slopes are different by over a factor of two; this reflects the distinct seasonal pattern in the ratios of the different hopanes to EC shown in Fig. 1c.

3.2. Ratio–ratio plots comparing ambient data and published source profiles

CMB analysis depends critically on the relative distribution of fitting species included in the model. In this section, we focus on the relative distribution of the five key motor vehicles markers—four hopanes and EC—that are included (*fitted*) in the CMB model. We do not include steranes in the analysis because not all source profiles report sterane emissions. Ambient data for the five motor vehicle markers can be compared to source profiles using two ratio–ratio plots: $S+R$ -homohopanes and $S+R$ -bishomohopanes normalized by norhopane (Figs. 3a and c); and norhopane and hopane normalized by EC (Figs. 3b and d).

The organization of the ambient data in the ratio–ratio plots provides significant insight into potential source profile combinations. In the winter, the ambient data of the five motor vehicle markers largely cluster to a point in the ratio–ratio plots shown in Figs. 3a and b; the modest variability in the wintertime hopanes-to-EC ratios (Fig. 3b) can largely be attributed to measurement uncertainty. Therefore, CMB can reproduce the wintertime concentrations of all five motor vehicle markers with a *single* source profile. In the summer, the hopane data cluster to a point in a ratio–ratio plot (Fig. 3c) but the hopanes-to-EC ratios are

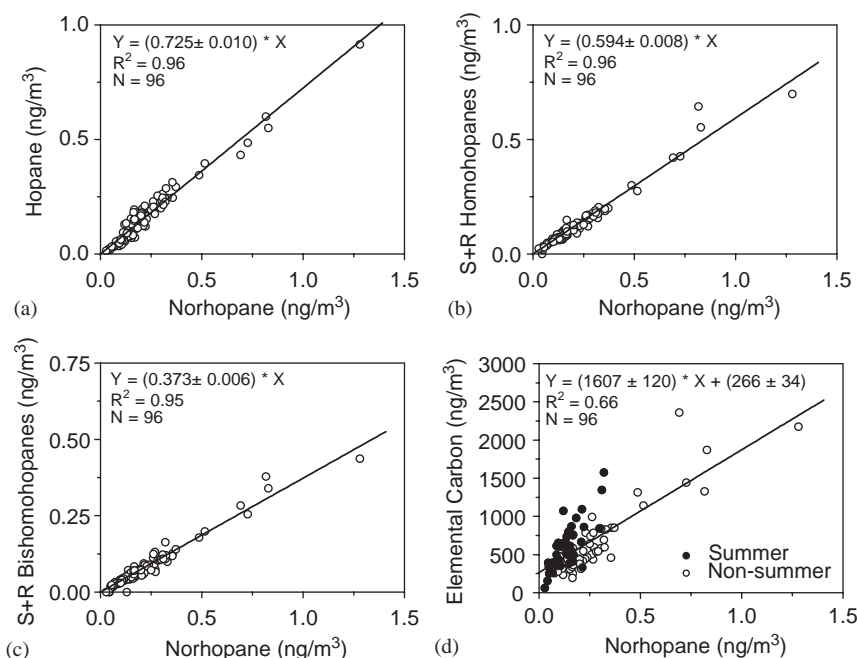


Fig. 2. Scatter plots of ambient concentrations of selected molecular markers and EC versus norhopane. Lines indicate linear regressions. In (d), the filled symbols represent the summer data, while the regression includes all the data points.

distributed along a line (Fig. 3d); therefore at least two source profiles are needed that bracket the ambient hopanes-to-EC ratios along the diagonal line defined by the summertime ambient data.

Source profiles are also shown in the ratio–ratio plots in Fig. 3. We consider gasoline and diesel profiles measured in the Denver, CO area as part of the Northern Front Range Air Quality Study (NFRAQS) (Watson et al., 1998a) and in Southern California (Schauer et al., 1999, 2002), as well as diesel profiles measured in Texas (Fraser et al., 2002). We do not consider the oxidation catalyst-fitted metro bus and diesel idling profiles reported by Fraser et al. (2002).

The most striking feature of the source profiles is the wide scatter of the different motor vehicle profiles compared to the well-organized ambient data (Fig. 3). The fact that the source profiles exhibit much more variability than the ambient data is not surprising. Each source profile represents the emissions from a single or small number of vehicles while the ambient data represent the aggregate emissions of the entire vehicle fleet. The well-organized ambient data indicate that atmospheric mixing averages out much of the vehicle-to-vehicle differences in emissions.

When comparing the different profiles (Fig. S1, Supporting Information), one must acknowledge

the potential effects of differences in testing procedures and analytical techniques used by different studies on the results. For example, the profiles reported by NFRAQS use the IMPROVE method to measure EC (Chow et al., 1993), while the others are based on the NIOSH protocol (NIOSH, 1999). Comparison studies have revealed significant differences in EC measurements using these two techniques (Chow et al., 2001), although more recent research indicates good agreement of EC measured in diesel exhaust samples using both protocols (Fujita et al., 2005). However, analytical issues must be kept in perspective because large variability exists for profiles measured using the same testing procedures and analytical techniques, e.g. the order-of-magnitude difference in the EC/OC ratios across the subset of profiles measured with either technique (Fig. S1). This indicates that actual variability in vehicle-to-vehicle emissions is much larger than differences associated with analytical techniques for either hopanes or EC.

The chemical composition of the emissions depends on a number of factors. For example, the relative distribution of the hopanes in emissions depends on the origin of the crude oil or other fossil fuel (Simoneit, 1984; Oros and Simoneit, 2000). Figs. 3a and c show that emissions from non-vehicular sources such as low-temperature coal

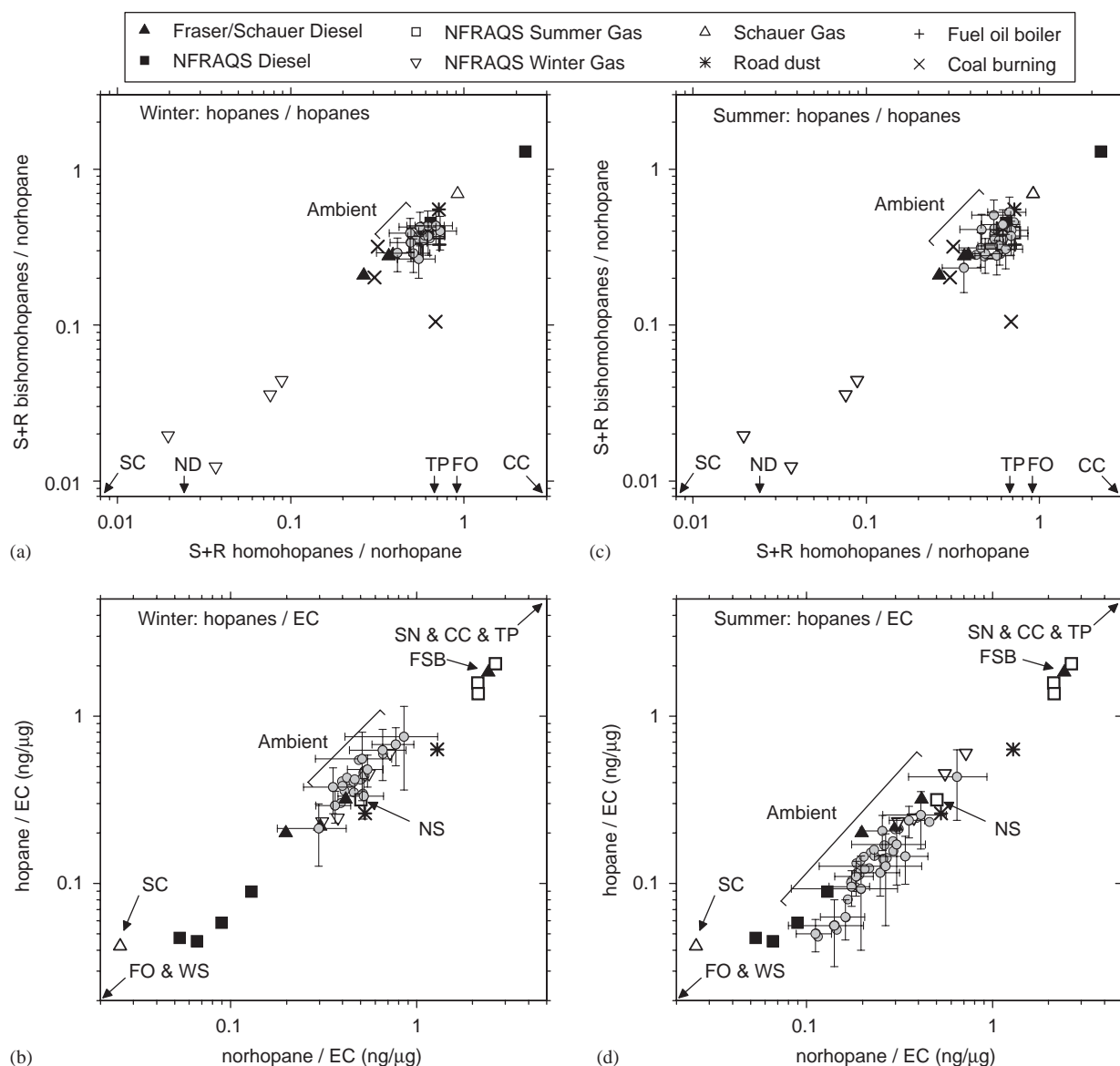


Fig. 3. Ratio-ratio plots comparing (a and b) winter and (c and d) summer ambient data to published source profiles. Gray circles are ambient data; solid symbols are diesel vehicle profiles, open symbols are gasoline vehicle profiles, and unclosed symbols are non-vehicular sources. Two- and three-character tags are labels for selected source profiles: “SC” is Schauer et al. (2002) catalytic gasoline profile; “FO” is fuel oil boiler (Rogge et al., 1997b); “WS” is wood smoke; “NS” is NFRAQS summer smoker (Watson et al., 1998a); “ND” is NFRAQS diesel profile (Watson et al., 1998a); “FSB” is Fraser et al. (2002) school bus; “SN” is Schauer et al. (2002) non-catalytic gasoline; “CC” is coal combustion (Oros and Simoneit, 2000); and “TP” is tar pots (Rogge et al., 1997a). Arrows pointing to axes indicate location of profiles located outside bounds of the plots. Propagated analytical and sampling uncertainties are shown as error bars for select ambient data.

combustion (Oros and Simoneit, 2000), fuel oil combustion (Rogge et al., 1997b) and tar pots (Rogge et al., 1997a) can have very different hopane distributions than motor vehicle emissions. This fact, coupled with the strong, seasonally invariant correlation between the ambient hopanes, is con-

sistent with a single dominant source for hopanes, presumably motor vehicles. Some of the variability in the source hopanes-to-EC ratios shown in Figs. 3b and d is related to engine technology; the diesel vehicle profiles are rich in EC with generally lower hopanes-to-EC ratios than gasoline vehicle

profiles. Notable exceptions are the Schauer et al. (2002) catalytic gasoline profile, which has lower hopanes-to-EC ratios than most of the diesel profiles, and the Fraser et al. (2002) diesel school bus profile, which has larger hopanes-to-EC ratios than most of the gasoline vehicle profiles. Within the set of NFRAQS gasoline vehicle profiles, smoking vehicles have lower hopanes-to-EC ratios than non-smoking vehicles and winter profiles have lower hopanes-to-EC ratios than summer profiles.

3.3. Developing fleet-average profiles

Although the source profiles are highly variable, the available profiles cluster by vehicle type in a manner that is largely consistent with a two-source CMB solution. In the winter, the hopanes-to-EC ratios of most diesel profiles are smaller than the ambient ratios while the hopanes-to-EC ratios of most gasoline vehicle profiles are larger than the ambient ratios (Fig. 3b). Therefore, the winter ambient data can be explained by almost any one of the diesel profiles (with the exception of the Fraser et al. (2002) school bus profile) paired with almost any one of the gasoline vehicle profiles (with the exception of the Schauer et al. (2002) catalytic gasoline and the NFRAQS smoker profiles). The modest day-to-day variability in the wintertime ratios of the different hopanes to EC can then be attributed to changes in the gasoline–diesel split.

The summer data are more problematic. While a similar combination of gasoline profiles with any one of the NFRAQS diesel profiles can explain the summertime hopanes-to-EC ratios, using the Schauer et al. (1999) and Fraser et al. (2002) diesel profiles for the summer data creates a number of challenges that are considered in a later section.

A major challenge for analyzing either the winter or summer data with CMB is selecting among the numerous CMB models based on different pairs of individual gasoline and diesel source profiles. The problem is that within the set of CMB models that produce statistically acceptable solutions large differences exist in the amount of OC apportioned to a given source class. These differences are primarily caused by differences in the marker-to-OC and marker-to-PM ratios of the source profiles included in the model. These ratios vary by more than an order of magnitude across the set of published vehicle profiles (Fig. S1, Supplementary Material).

Marker-to-OC and marker-to-PM ratios are critical because CMB calculates source strengths based on an optimized “best-fit” of the set of marker compounds included in the model. OC or PM_{2.5} mass is not directly included (or *fitted*) in the model for CMB analysis with molecular markers because “source profiles” for secondary organic aerosols are not known. CMB models based on source profiles with small marker-to-OC ratios (e.g. the NFRAQS smoker profiles) will apportion more OC to a given source class than profiles with larger marker-to-OC ratios (e.g. the NFRAQS low-emitters). For example, across the set of NFRAQS profiles the ambient OC apportioned to gasoline vehicles varies by more than a factor of three depending on the specific gasoline vehicle profile included in the model.

Another issue associated with using individual profiles is that these profiles are developed for a particular type of vehicle, e.g. low-emitter gasoline, which may not be representative of the emissions from the entire fleet. Therefore we combine the available profiles to create more representative fleet-average profiles. In order to account for any potential issues associated with testing procedures and analytical techniques used by different research groups we develop two sets of profiles: one based on the research by Schauer and Fraser and a second based on the NFRAQS data. We consider only the NFRAQS summer gasoline profiles, since for the winter gasoline profiles many of the compounds were near detection limits (Cadle et al., 1999b).

To develop fleet average gasoline vehicle profiles, we use information from the 2001 National Household Travel Survey (<http://nhts.ornl.gov/2001/>), which describes the vehicle fleet in terms of vehicle age and estimated “vehicle miles traveled” (VMT). Although this is a national survey, we assume the results are applicable to the Pittsburgh aerosol given the significance of regional transport that combines emissions across a large spatial domain. While other factors such as maintenance history likely play a role in emissions, we follow the approach of Cadle et al. (1999a) and assume that vehicle age is a reasonable metric for emissions.

Three fleet average gasoline profiles are constructed using the NFRAQS data. The “middle-ground” estimate uses the low-emitter profile to represent vehicles less than 5 years old (43.5% of the VMT), the medium-emitter profile to represent vehicles between 5 and 15 years of age (49.6% of VMT), and an average of the smoker and

high-emitter profiles to represent vehicles older than 15 years (6.8% of VMT). To test the sensitivity of the CMB results, we also use fleet compositions with smokers/high-emitters comprising 1% and 12% of VMT as two extreme fleet compositions.

The second set of fleet average gasoline profiles is based on the Schauer et al. (2002) gasoline profiles. The low and medium emitters are represented by the Schauer et al. (2002) catalytic gasoline profile and high emitters/smokers by the Schauer et al. (2002) non-catalytic gasoline profile. In this case, we consider only two vehicle fleets, one with 1% smokers/high emitters and a second with 12% smokers/high emitters.

To estimate the diesel vehicle contribution, we consider two diesel profiles. The Schauer–Fraser average diesel profile consists of the Class 8 truck Fraser et al. (2002) profile (the emission rates from the two reported profiles are averaged into a single profile) and the Schauer et al. (1999) medium-duty profile (a composite sample from two vehicles). We assume that each profile represents an equal fraction of the diesel fleet. The second profile is the NFRAQS heavy-duty diesel profile “N048”, a

composite of 10 vehicles (Watson et al., 1998a)—this is the “NFRAQS Heavy-duty 1 (W)” profile shown in Fig. S1.

The five fleet-average gasoline and two diesel profiles are plotted with the ambient data on the ratio–ratio plots of Fig. 4. Separate plots are shown to illustrate the seasonal shifts in the ambient data relative to the source profiles. These shifts are discussed in a later section. The summer plots also present the Schauer et al. (2002) catalytic and non-catalytic gasoline profiles separately without averaging. The average profiles are listed in Table S2 (Supplementary Material).

3.4. CMB analysis of the wintertime data

The five fleet-average gasoline profiles combined with the two different diesel profiles result in 10 different scenarios for CMB analysis of the wintertime data. All of these combinations yield statistically acceptable solutions on all winter days; for example, the median R^2 values are 0.92 or 0.93 while median χ^2 values range between 2.0 and 2.4, with 13–17 degrees of freedom (DF) (the minimum

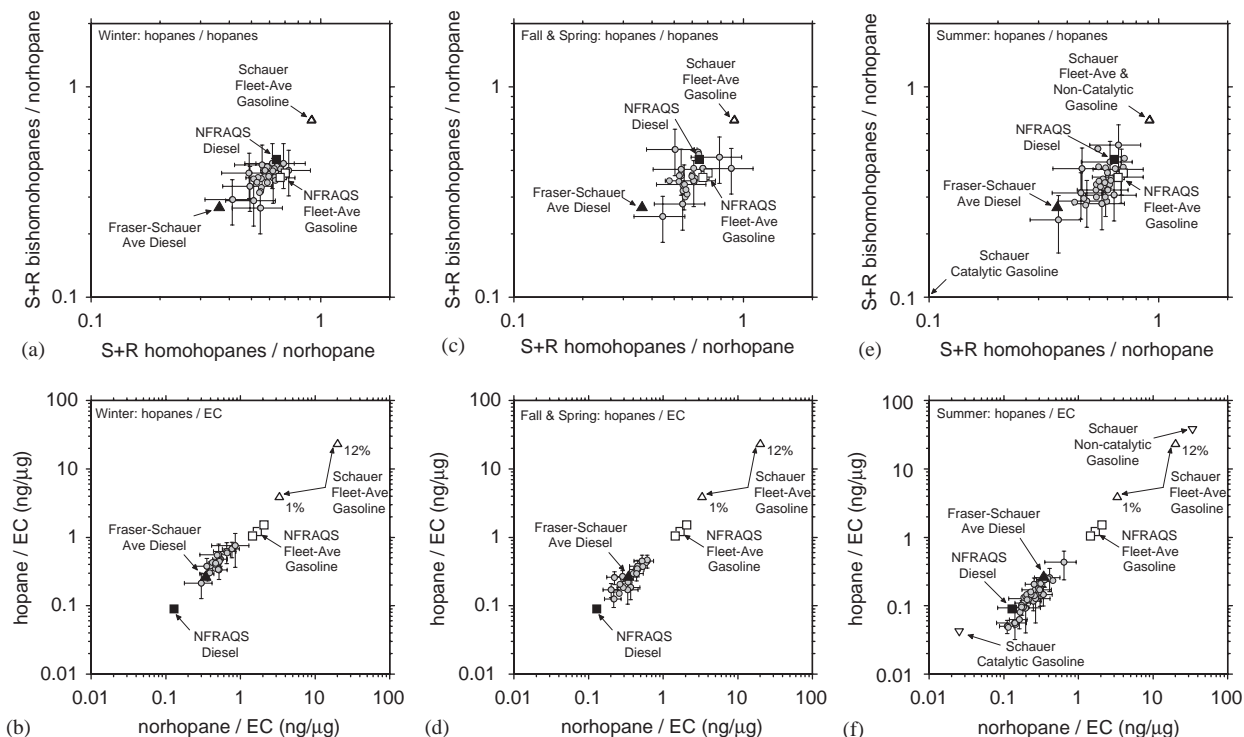


Fig. 4. Ratio–ratio plots showing different CMB scenarios and ambient data for the (a and b) winter, (c and d) spring and fall, and (e and f) summer. Gray circles are ambient data; solid symbols are diesel vehicle profiles and open symbols are gasoline vehicle profiles. Error bars on select ambient data represent the propagated analytical and sampling uncertainties.

confidence level for any given day is 98%). The *T*-statistics of the source contribution estimate (SCE) for the motor vehicle profiles are greater than 2.0 on over 85% of the days. Therefore, these statistical parameters provide little guidance for selecting among the 10 different statistically acceptable solutions.

Time series of the ambient OC apportioned to motor vehicle exhaust are shown in Fig. 5a. All of the solutions exhibit some day-to-day variability due to changes in ambient marker concentrations. The different solutions are also strongly correlated with one another as illustrated by the scatter plots shown in Fig. 6 which compare the daily OC apportioned to all vehicles, diesel vehicles and gasoline vehicles, and the gasoline–diesel split by two different scenarios.

Fig. 5a indicates that all 10 wintertime scenarios apportion a similar amount of ambient OC to motor vehicle emissions. The average total-vehicle OC estimated by the 10 different scenarios are all within a factor of 1.5 and are not statistically different based on the standard error estimates calculated by CMB (e.g. Fig. 6a). The NFRAQS diesel plus the NFRAQS 1% high-emitter/smoker gasoline scenario predicts the lowest average total-vehicle OC, $274 \pm 56 \text{ ng-Cm}^{-3}$ (\pm average standard error), while the NFRAQS diesel plus 1% non-catalytic Schauer gasoline scenario predicts the highest, $416 \pm 72 \text{ ng-Cm}^{-3}$. These predictions correspond to 13.4% and 20.3%, respectively, of the ambient OC in the wintertime. Therefore, we conclude that the total contribution of motor vehicles to ambient OC in the wintertime is well constrained. However, we must emphasize that the solutions are well constrained because we are performing analysis with fleet-averaged profiles. As previously discussed one can find a wider range of solutions if one considers individual profiles such as a smoker profile. Therefore, information regarding fleet composition (which profiles are included in the model) provides a critical constraint when considering all statistically acceptable CMB solutions.

Time series of the ambient OC apportioned to diesel vehicles, gasoline vehicles, and the gasoline–diesel split are shown in Figs. 5c–e, respectively. The median wintertime ratio of gasoline vehicle OC to diesel OC estimates varies between 0.63 and 2.90, indicating that some solutions predict diesel emissions dominate while others predict the opposite. The differences in gasoline–diesel split are often greater than the standard errors calculated by CMB,

as illustrated by the scatter plot shown in Fig. 6c. Therefore, there is little agreement among the solutions regarding the relative contribution of gasoline vehicles and diesel vehicles to ambient OC.

The key factor determining the gasoline–diesel split is which diesel vehicle profile is included in the model. Fig. 5e shows that all simulations using the Schauer–Fraser diesel profile indicate that diesel vehicle emissions are dominant, while gasoline vehicles dominate all simulations based on the NFRAQS diesel profile. The reason for this shift can be understood by closely examining how CMB determines the contribution of gasoline and diesel vehicles to ambient OC.

All of the scenarios identify diesel emissions as the dominant source of EC, contributing on average between 67% and 94% of the ambient EC (Fig. 7a). This means that the contribution of diesel emissions is essentially constrained by ambient EC levels, and the diesel OC depends strongly on the EC/OC ratio of the different diesel profiles. The EC/OC ratio of the NFRAQS diesel profile is 3.7 versus 2.1 for the Schauer–Fraser average profile, which explains why CMB calculations using the Schauer–Fraser profile estimate almost twice as much diesel OC as the NFRAQS diesel profile (Fig. 6b).

The amount of OC apportioned to gasoline vehicles depends on (a) the ambient hopanes not apportioned to diesel sources and thus available for gasoline apportionment, and (b) the hopanes-to-OC ratios of the gasoline vehicle profile. Since EC constrains the diesel contribution, the “leftover” hopanes (ambient hopanes minus hopanes apportioned to diesel vehicles) is determined by the hopanes-to-EC ratios of the diesel profile.

The hopanes-to-EC ratios of the Schauer–Fraser average diesel profile are two to three times higher than the NFRAQS diesel profile. The result is that CMB apportions significantly more of the hopanes to diesel vehicles when the Schauer–Fraser average diesel profile is included in the model, as illustrated in Fig. 7b. On average, the Schauer–Fraser diesel profile contributes 50–62% of the wintertime ambient norhopane compared to 20–26% by the NFRAQS diesel profile. Hence, given the same gasoline profile, a CMB solution based on the NFRAQS diesel profile apportions more OC to gasoline vehicles than a solution based on the Schauer–Fraser diesel profile. As discussed earlier, the NFRAQS diesel profile also apportions less OC to diesel sources than the Schauer–Fraser diesel profile.

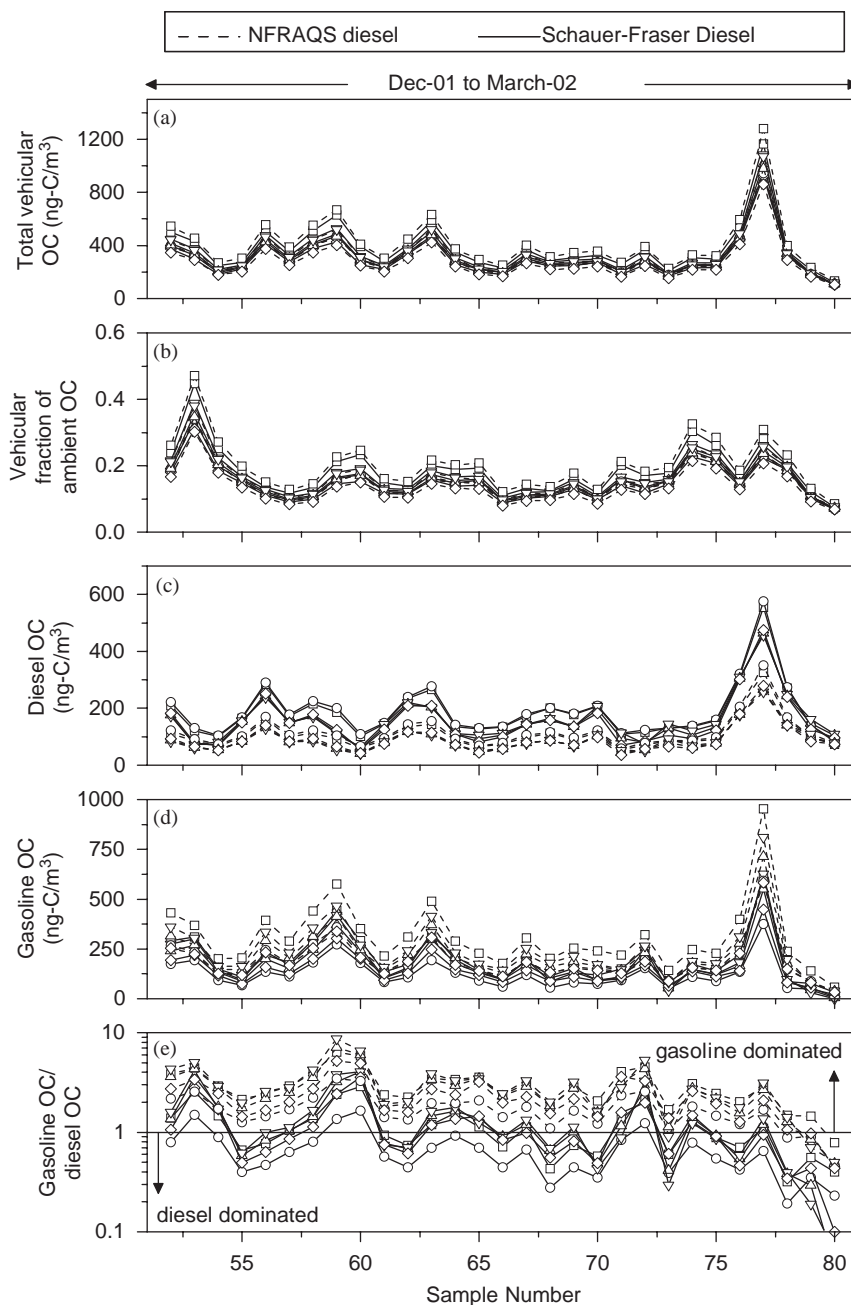


Fig. 5. Time series of CMB solutions for the winter: (a) total vehicular OC, (b) total vehicular OC as a fraction of ambient OC, (c) gasoline vehicle OC, (d) diesel vehicle OC, and (e) ratio of gasoline OC to diesel OC. Solid lines are calculations using the Schauer–Fraser average diesel profile; dashed lines are calculations using NFRAQS diesel profile. Symbols indicate different fleet-average profiles for gasoline vehicles: □ 1% high-emitter Schauer gasoline; ○ 12% high-emitter Schauer gasoline; ◇ 1% high-emitter NFRAQS gasoline; △ 6.8% high-emitter NFRAQS gasoline; and ▽ 12% high-emitter NFRAQS gasoline.

The effect of the hopanes-to-OC ratios of the different gasoline profiles can be seen by comparing the predicted gasoline-vehicle OC across a set of calculations performed with the same diesel profile.

Fixing the diesel profile means that the amount of hopanes apportioned to gasoline vehicles is essentially constant. Therefore, the factor-of-1.6 variation in the amount of gasoline vehicle OC is caused

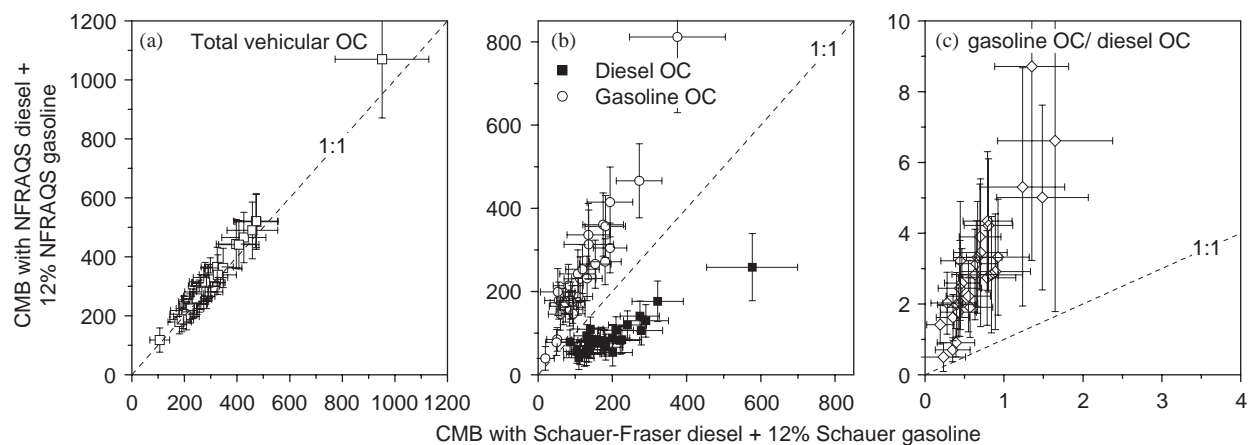


Fig. 6. Scatter plots comparing estimated (a) total vehicular OC (ng-C m^{-3}), (b) gasoline and diesel OC (ng-C m^{-3}), and (c) gasoline–diesel split for two different wintertime CMB solutions. “12% Schauer gasoline” is the 12% high-emitter composite profile based on the gasoline profiles of Schauer et al. (2002). “12% NFRQS gasoline” is the 12% high-emitter composite profile based on the NFRQS data (Watson et al., 1998a). The error bars indicate the standard errors calculated by CMB.

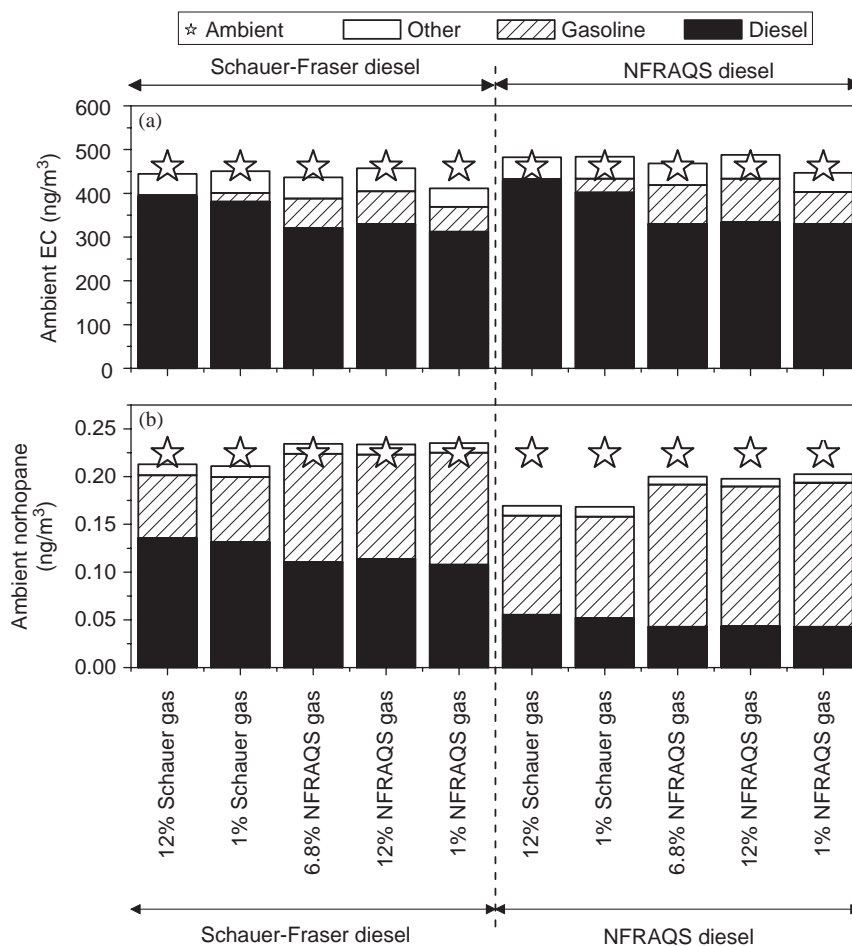


Fig. 7. Average wintertime apportionment of (a) EC and (b) norhopane by the 10 different CMB scenarios.

by differences in the hopane-to-OC ratios of the different fleet-average gasoline profiles. As previously discussed, over a factor of three variation is observed if one considers individual gasoline profiles as opposed to the fleet average profiles.

3.5. CMB analysis of the summertime data

Constructing scenarios to explain the summertime data with its wide range of hopanes-to-EC ratios creates a number of challenges. Robinson et al. (2006a) argues that the seasonal changes in these ratios are caused by photochemical oxidation of hopanes in the regional air mass. If true, the CMB model cannot be used to analyze the summertime data because the assumption that the compounds included in the model are conserved during transport is no longer valid. However the stability of molecular markers in the context of regional transport remains an open question. Therefore, in this section, we apply the CMB model to analyze the summertime data, implicitly assuming that the molecular markers included in the model are conserved.

As noted previously, Figs. 3c and d indicate that the well-organized summertime data are consistent with a two-source solution, but there are few viable source profile combinations that can explain the ambient hopane-to-EC ratios. Notably the Schauer et al. (1999) and Fraser et al. (2002) diesel profiles have larger hopane-to-EC than the summertime data. Only the NFRAQS diesel profiles and the Schauer et al. (2002) catalytic gasoline profile bracket the low end of the summertime data in Fig. 3d. Since non-vehicular sources contribute little EC in the summer (Robinson et al., 2006a,c), the ambient data require pairing one of the NFRAQS diesel profiles with one of the many gasoline profiles located in the upper right-hand corner of Fig. 3d.

Alternatively, the summertime data can be explained by pairing either the Fraser et al. (2002) or Schauer et al. (1999) diesel profiles with the Schauer et al. (2002) catalytic gasoline profile. However, this combination cannot explain the ambient bishomohopane and homohopane ratios (Fig. 4e). One possibility is to also include the Schauer et al. (2002) non-catalytic gasoline profile in the model, which would also account for emissions from high-emitting gasoline vehicles. However, Figs. 4e and f indicate that Schauer–Fraser average diesel profile is located on the mixing line connecting the two Schauer et al. (2002) gasoline profiles. To resolve the three motor vehicle profiles requires

additional markers, so we add tetracosane (C24) and hexacosane (C26) as fitting species in our CMB model. Schauer et al. (1996) estimate that for Los Angeles, CA in 1982, vehicular emissions contributed about half or more of the lower carbon number *n*-alkanes (C23–C27). We do not fit pentacosane (C25) because there is a marked preference for the odd *n*-alkanes primarily in the summertime Pittsburgh data, indicative of a strong biogenic influence over the odd *n*-alkanes (Simoneit, 1986).

The summertime data are analyzed with six scenarios: the NFRAQS diesel profile paired with one of the five fleet-average gasoline vehicle profiles (the NFRAQS scenarios), and the Schauer–Fraser average diesel profile paired with the Schauer et al. (2002) catalytic and non-catalytic gasoline profiles (the Schauer–Fraser scenario). All six summertime solutions are statistically acceptable, with median R^2 values of 0.93, median χ^2 values of 1.9 or 2.0 and 12–18 degrees of freedom (DF) for the five NFRAQS scenarios; and a median R^2 value of 0.89, median χ^2 3.9, and 13–18 DF for the Schauer–Fraser model. The minimum confidence level based on the χ^2 and DF is 96% across all scenarios except for 2 (out of 41) days with the Schauer–Fraser scenario. Therefore the CMB goodness-of-fit parameters provide little guidance in selecting among the different solutions.

Time series of results from the summertime solutions are shown in Fig. 8. On average, the Schauer–Fraser scenario apportions 31% of the ambient OC to motor vehicle emissions, five to six times that apportioned by the NFRAQS scenarios (4.9–5.8%). Figs. 8c and d indicate that the primary difference between the two scenarios is the amount of OC apportioned to gasoline vehicles. The Fraser–Schauer scenario apportions about 20 times more OC to gasoline sources (average 28% of ambient OC) than the NFRAQS scenarios (average less than 2% of ambient OC to gasoline sources). This difference is much larger than the standard errors calculated by CMB. Fig. 8c indicates that there is significant day-to-day variation in the amount of gasoline vehicle OC predicted by the Schauer–Fraser scenario; on some days gasoline vehicles contribute almost no OC, while on other days they contribute more than $2\mu\text{g-C m}^{-3}$. Such large variations are not expected given the modest day-to-day variability in vehicle activity.

The Fraser–Schauer scenario is dominated by the Schauer et al. (2002) catalytic gasoline profile which contributes 78% of the vehicular OC and 27% of

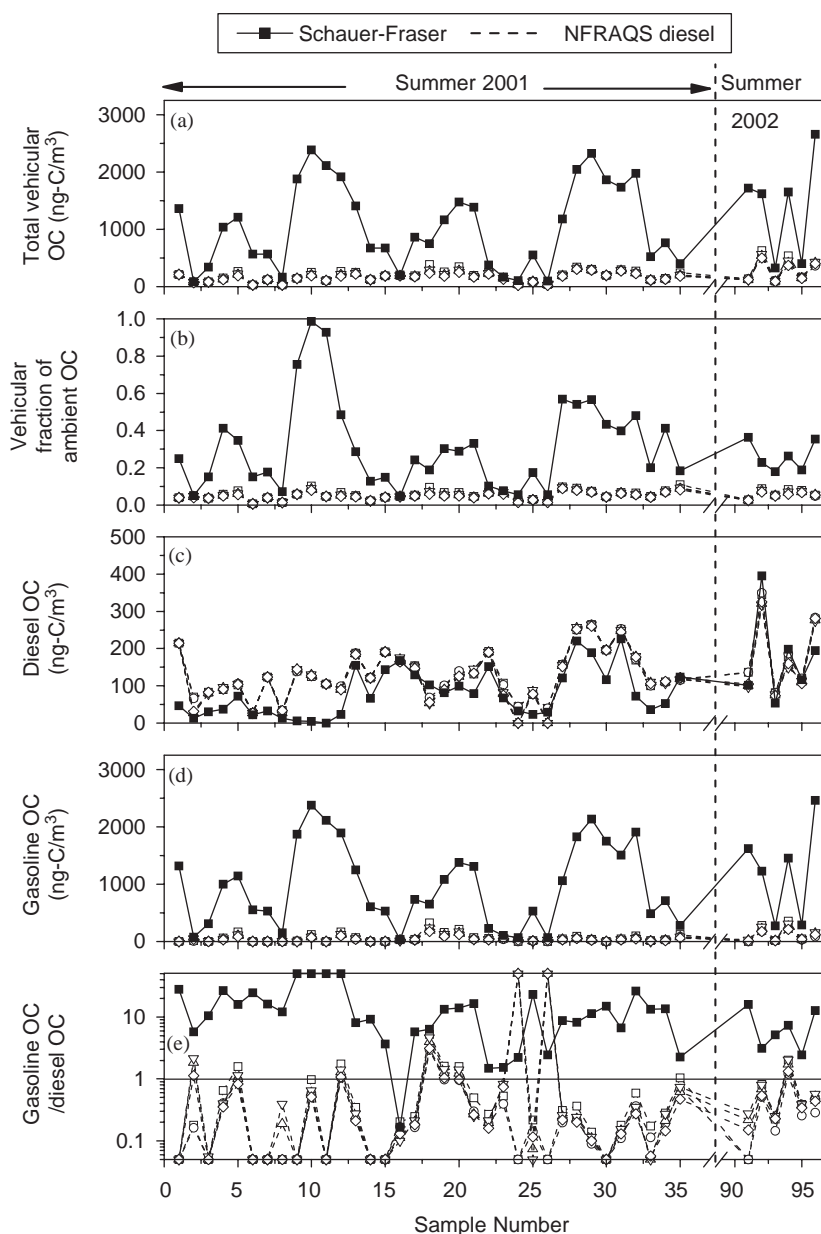


Fig. 8. Time series of CMB solutions for the summer: (a) total vehicular OC, (b) total vehicular OC as a fraction of ambient OC, (c) gasoline vehicle OC, (d) diesel vehicle OC, and (e) ratio of gasoline OC to diesel OC. Dashed lines are calculations using NFRAQS diesel profile with symbols indicating different fleet-average profiles for gasoline vehicles: \square 1% high-emitter Schauer gasoline; \circ 12% high-emitter Schauer gasoline; \diamond 1% high-emitter NFRAQS gasoline; \triangle 6.8% high-emitter NFRAQS gasoline; and ∇ 12% high-emitter NFRAQS gasoline. In (e) points plotted on axis have a gasoline–diesel split of greater than 50 (i.e. diesel OC is zero) or less than 0.05.

the ambient OC. This occurs for two reasons. First, the ratios of the different hopanes to OC (marker-to-OC ratios) of the Schauer et al. (2002) catalytic gasoline profile are an order of magnitude lower than any of the other vehicle profiles (Fig. S1). These extremely low ratios allow this profile to dominate the OC apportionment while only con-

tributing on average just 4.2% of the ambient norhopane. Second, this scenario includes the *n*-alkanes tetracosane and hexacosane as fitting species, which are predominantly apportioned to the catalytic gasoline profile. Note that the Schauer–Fraser scenario cannot be implemented for the summer data without fitting the *n*-alkanes.

The fact that the Schauer–Fraser scenario is dominated by a catalytic gasoline profile with a low emission rate is unexpected because “high emitters” are thought to be the dominant source of emissions, e.g. Beaton et al. (1995). Given its low OC emission rate, the Schauer et al. (2002) catalytic gasoline profile will only influence the fleet average gasoline source profile if it represents a super-majority of the vehicle fleet. Since the very low hopanes-to-OC ratios of the Schauer et al. (2002) catalytic gasoline profile appear to be an outlier compared to all of the other vehicular source profiles (Fig. S1), the Schauer–Fraser scenario likely overestimates the actual contribution of gasoline vehicles to the ambient OC.

There are also concerns with the summertime NFRAQS solutions; most notably, the large day-to-day changes in the gasoline–diesel split. Fig. 8e indicates that on many summertime days diesel vehicles dominate the gasoline–diesel split while on others the split is more even. These changes are primarily associated with changes in the amount of gasoline vehicle OC. Previous studies have observed weekday–weekend patterns in the influence of gasoline and diesel vehicles on ambient air quality (Harley et al., 2005); however, the shifts shown in Fig. 8e do not follow any discernable pattern. In addition, the summertime shifts in the gasoline–diesel splits are much greater (relative standard deviation of 147–166%, Fig. 8e) compared to the winter (RSD 40–62%, Fig. 5e), as the CMB model has to account for the widely varying summertime hopane-to-EC ratios.

3.6. Seasonal patterns in source apportionment

CMB models which include the NFRAQS diesel profile paired with a gasoline profile can explain the entire dataset; however all of these solutions show strong seasonal changes in the OC apportioned to motor vehicles. The driver for the seasonal changes is the ambient ratios of hopanes-to-EC—the average hopanes-to-EC ratios in the summer are almost a factor of 3 lower than those in the winter (Fig. 1c). Therefore, with the NFRAQS diesel-based scenarios, diesel vehicle emissions dominate in the summer (Fig. 8e) and gasoline vehicle emissions dominate in the winter (Fig. 5e) in order for CMB to match the observed seasonal patterns in the ambient hopanes-to-EC ratios. A similar seasonal pattern in the gasoline–diesel split has been estimated using CMB

and molecular markers in the Southeastern US (Zheng et al., 2002).

There are a number of potential explanations for seasonally varying ambient hopanes-to-EC ratios. These include seasonal changes in source activity; seasonal changes in the fleet composition; seasonal changes in the source emission factors; and photochemical aging of the hopanes. All of these explanations are discussed in detail in Robinson et al. (2006a) and the first two are relatively easy to dismiss. Some of the scatter in the hopanes-to-EC ratio might be due to issues with EC measurements (Chow et al., 2001; Subramanian et al., 2006); however, there is no evidence that these problems are sensitive to seasonal factors.

Seasonal variations in the organic composition of motor vehicle emissions and photochemical decay of hopanes provide the two most likely explanations of the seasonality in the hopanes-to-EC ratios. To explain the ambient data, the motor vehicle emissions of hopanes relative to EC would need to be higher in the winter compared to the summer—seasonally shifting the location of the source profiles shown in the Figs. 3b and d. Alternatively the hopanes-to-OC ratio of the emissions could shift seasonally, changing the amount of OC apportioned to the different sources. However, seasonally shifting profiles would not explain the significant day-to-day variations in the summertime hopanes-to-EC ratio which cause the large day-to-day changes in the gasoline–diesel split shown in Fig. 8e.

At present little is known about seasonal variability in the organic composition of motor vehicle emissions. In Pittsburgh, temperatures are much colder in the winter than in the summer; gasoline composition also varies seasonally with reformulated gasoline used in the summer ozone season. Both of these factors likely influence emissions. Two studies have measured warm and cold-weather gasoline vehicle emission profiles with speciated organics data (Watson et al., 1998a; Zielinska et al., 2004). The cold weather profiles measured by both studies have lower hopanes-to-EC ratios than the warm weather profiles—the opposite of what would be required to explain the ambient data. In fact, Fig. 3b indicates that the hopanes-to-EC ratios of the winter NFRAQS gasoline profiles are lower than the winter PAQS ambient data. The result is that CMB cannot find solutions for many of the winter days if the published cold weather profiles are used in the model. As for diesel emissions, there could be seasonal changes in the lubricating oil used in diesel

engines. The NFRAQS results do not include heavy-duty diesel tests from the summer, but our CMB solutions already use a *winter* NFRAQS diesel profile. More source testing is needed to determine if there are significant seasonal variations in the vehicular emission factors of OC, EC, and the hopanes.

Photochemical oxidation of the hopanes during long-range transport is another potential explanation for the lower and widely varying hopanes-to-EC ratios in the summer. When considering oxidation as a potential explanation, one must acknowledge the significant differences between Pittsburgh (and other areas in the Eastern United States) and Los Angeles, where the molecular marker techniques were developed. Air pollution in the Los Angeles basin is dominated by local emissions mixed with fairly clean background air over relatively short transport distances, while air quality in many other areas of the country is dominated by regional transport. Regional transport allows significant time for atmospheric processing of the emissions. Therefore, one might expect hopanes to be depleted in the regional air mass, particularly in summer when oxidant levels are higher. This is exactly what is shown by measurements made in Pittsburgh and at an upwind rural site (Robinson et al., 2006a), and it is difficult to explain this observation with seasonally varying emission profiles. The widely varying summertime ratios are also consistent with photochemistry; for example, photochemistry is likely to be less important after periods of rain when local emissions are more significant. If oxidation is important, it likely reduces concentrations of all of the reduced organic compounds used as molecular markers in CMB, not just the hopanes.

Fall and spring data are shown in Figs. 4c and d. Comparing the different ratio–ratio plots in Fig. 4 indicates that the fall and spring data lie in between the summer and winter extremes. In particular, there is more variability in the ratio of the different hopanes to EC in the fall and spring than in the winter but less than in the summer (Robinson et al., 2006a). CMB analysis of the fall and spring data shows some shifting of the gasoline–diesel split towards diesel relative to the winter.

3.7. Source apportionment of fine particle mass

To estimate the contribution of motor vehicle emissions to fine particle mass, CMB analysis was

also performed with source profiles normalized by $\text{PM}_{2.5}$ mass emissions. On a $\text{PM}_{2.5}$ mass basis, the CMB results exhibit the same variability as the OC apportionment because the source profile marker-to- $\text{PM}_{2.5}$ -mass ratios exhibit essentially the same amount of variability as the marker-to-OC ratios (Figure S1). Normalizing profiles with $\text{PM}_{2.5}$ mass also does not alter the previously discussed seasonality of the solutions; this pattern is driven by the seasonal shift in the ambient hopanes/EC data and not the marker-to-OC or marker-to- $\text{PM}_{2.5}$ -mass ratios of the source profiles.

In wintertime, the amount of $\text{PM}_{2.5}$ mass apportioned to motor vehicle emissions by the 10 different CMB scenarios varies by a factor of 1.4 with an average contribution of $850 \pm 89 \text{ ng m}^{-3}$ of $\text{PM}_{2.5}$ mass (average \pm standard deviation of the results from the ten scenarios). Therefore, the wintertime CMB estimates of the contribution of vehicular emissions to ambient $\text{PM}_{2.5}$ mass are as well constrained as the estimates to OC shown in Fig. 5a. However, the summertime solutions for $\text{PM}_{2.5}$ mass show the same wide divergence as the OC results shown in Fig. 8.

There are some interesting differences between the CMB solutions for $\text{PM}_{2.5}$ mass compared to those for OC, especially related to the gasoline–diesel split. For example, the NFRAQS diesel-based CMB scenarios apportion 449 ± 184 to $581 \pm 172 \text{ ng m}^{-3}$ of $\text{PM}_{2.5}$ mass in the wintertime to diesel vehicles versus only 239 ± 49 to $500 \pm 108 \text{ ng m}^{-3}$ of $\text{PM}_{2.5}$ mass to gasoline vehicles. The median gasoline–diesel split (the ratio of gasoline contribution to diesel contribution) for the five NFRAQS diesel-based CMB solutions is between 0.42 and 0.93 on a $\text{PM}_{2.5}$ mass basis versus between 1.69 and 2.90 on an OC basis (Fig. 5e). Therefore, on an OC basis gasoline vehicles dominate the gasoline–diesel split while diesel vehicles dominate the split on a $\text{PM}_{2.5}$ mass basis. Results for the Schauer–Fraser diesel-based CMB scenarios are even more skewed to diesel dominance on a $\text{PM}_{2.5}$ mass basis, with median gasoline–diesel splits between 0.23 and 0.54 on a $\text{PM}_{2.5}$ mass basis. This apparent shift in the gasoline–diesel split simply reflects the fact that diesel emissions are dominated by EC and gasoline vehicle emissions by OC. For example, the NFRAQS average gasoline profile with 12% smokers/high emitters has a $\text{PM}_{2.5}$ -mass-to-OC ratio of 1.7, compared to ~ 5 for the NFRAQS diesel profile. This difference is accounted for in the marker-to- $\text{PM}_{2.5}$ -mass ratios of the source profiles.

4. Conclusions

This paper has illustrated some of the strengths and challenges associated with performing CMB analysis with molecular markers in the context of apportioning motor vehicle emissions. A significant strength of the approach is the strong correlations in the ambient molecular marker concentrations. These correlations reflect the high source specificity of certain organic species and imply the existence of well-defined source profiles, even in Pittsburgh, a location strongly influenced by regional transport. However, a major challenge is the variability in the source profiles. The motor vehicle profiles are much more variable than the ambient data, which creates significant uncertainty in the CMB estimates.

The marker-to-OC ratios are a critical parameter in determining the amount of OC apportioned to a source profile. In sum, the molecular markers fitted in the CMB model typically contribute less than 5% of the OC mass, which means that the marker-to-OC ratios can be highly variable as illustrated by the order-of-magnitude variability in these ratios among the set of published vehicle profiles (Fig. S1). This variability and its consequent effects on predicted fleet emissions must be carefully considered when evaluating CMB solutions. In particular, the divergence in different solutions caused by this variability is often greater than sampling and analytical uncertainties propagated by CMB (Fig. 6). The statistical measures calculated by CMB do not account for the variability in marker-to-OC ratios; therefore profile-to-profile differences in these ratios can create uncertainties in the source strength estimates that are extremely hard to remove. The same problems exist if one performs CMB analysis to apportion $\text{PM}_{2.5}$ mass. In this paper, we have reduced the effect of marker-to-OC ratios by constructing fleet-average profiles from the set of published profiles.

In the winter, the total amount of vehicular OC is well constrained, contributing on average between 13% and 20% of the ambient OC (274 ± 56 – $416 \pm 72 \text{ ng m}^{-3}$). However, source profile variability creates uncertainty in the gasoline–diesel split. On an OC basis, the NFRAQS diesel-based CMB solutions estimate a gasoline-dominated vehicular contribution while the Schauer–Fraser diesel-based CMB models suggest either the opposite or a more even split. On a $\text{PM}_{2.5}$ mass basis, all solutions indicate that diesel emissions tend to dominate the

gasoline–diesel split, but there is almost a factor-of-five variability in the split. Variability in the EC and hopanes source emission rates is the main contributor to this uncertainty. Additional source profiles and/or motor vehicle markers are needed to better constrain the gasoline–diesel split. It should also be noted that the winter results for total vehicular OC are well-constrained only because we did not consider the wintertime results from the CMB model which includes the two Schauer et al. (2002) gasoline profiles as separate sources (the Schauer–Fraser scenario described in Section 3.5). This model produces statistically acceptable solutions throughout the year, but, like in the summer, estimates very high contributions of gasoline vehicle OC, and over-apportions the ambient OC on several winter days (by as much as 73%).

Explaining the summer data with its widely varying hopanes-to-EC ratios is problematic. Although CMB can find statistically acceptable solutions for the summer, there is little agreement among the different scenarios even for the total vehicular contribution (unlike in the winter). The average summer contribution varies from 5% to 31% (176 ± 49 to $1091 \pm 363 \text{ ng m}^{-3}$) of the ambient OC. Therefore, we have little confidence in the CMB solutions for the contribution of motor vehicles to Pittsburgh OC or the gasoline–diesel split during the summer. More research is needed to better understand the seasonal variability of source profiles and the photochemical stability of molecular markers under conditions of significant regional transport.

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Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2006.06.055](https://doi.org/10.1016/j.atmosenv.2006.06.055).

References

- Beaton, S.P., Bishop, G.A., Zhang, Y., Ashbaugh, L.L., D. Lawson, R., Stedman, D.H., 1995. On-road vehicle emissions—regulations, costs, and benefits. *Science* 268 (5213), 991–993.
- Cadle, S.H., Mulawa, P., Hunsanger, E.C., Nelson, K., Ragazzi, R.A., Barrett, R., Gallagher, G.L., Lawson, D.R., Knapp, K.T., Snow, R., 1999a. Light-duty motor vehicle exhaust particulate matter measurement in the Denver, Colorado area. *Journal of the Air & Waste Management Association* 49, 164–174.
- Cadle, S.H., Mulawa, P.A., Hunsanger, E.C., Nelson, K., Ragazzi, R.A., Barrett, R., Gallagher, G.L., Lawson, D.R., Knapp, K.T., Snow, R., 1999b. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. *Environmental Science and Technology* 33 (14), 2328–2339.
- Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI thermal optical reflectance carbon analysis system—description, evaluation and applications in united-states air-quality studies. *Atmospheric Environment Part A—General Topics* 27 (8), 1185–1201.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., Merrifield, T., 2001. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Science and Technology* 34 (1), 23–34.
- Fraser, M.P., Lakshmanan, K., Fritz, S.G., Ubanwa, B., 2002. Variation in composition of fine particulate emissions from heavy-duty diesel vehicles. *Journal of Geophysical Research—Atmospheres* 107 (D21), in press. [doi:10.1029/2001JD000558](https://doi.org/10.1029/2001JD000558).
- Fraser, M.P., Buzcu, B., Yue, Z.W., McGaughey, G.R., Desai, N.R., Allen, D.T., Seila, R.L., Lonneman, W.A., Harley, R.A., 2003a. Separation of fine particulate matter emitted from gasoline and diesel vehicles using chemical mass balancing techniques. *Environmental Science and Technology* 37 (17), 3904–3909.
- Fraser, M.P., Yue, Z.W., Buzcu, B., 2003b. Source apportionment of fine particulate matter in Houston, TX, using organic molecular markers. *Atmospheric Environment* 37 (15), 2117–2123.
- Fujita, E.M., Zielinska, B., Arnott, W.P., Campbell, D.E., 2005. Chemical characterization of mobile source emissions—relation to ambient measurements in vehicle dominated and urban background locations. particulate matter supersites program and related studies, Abstract 4A–2. Particulate Matter Supersites Program and Related Studies: An AAAR International Speciality Conference, Atlanta, GA, p. 27.
- Harley, R.A., Marr, L.C., Lehner, J.K., Giddings, S.N., 2005. Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition. *Environmental Science and Technology* 39 (14), 5356–5362.
- NIOSH, 1999. Elemental Carbon (Diesel Particulate): Method 5040 <<http://www.cdc.gov/niosh/nmam/pdfs/5040f3.pdf>>.
- Oros, D.R., Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel* 79 (5), 515–536.
- Pekney, N.J., Davidson, C.I., 2005. Determination of trace elements in ambient aerosol samples. *Analytica Chimica Acta* 540 (2), 269–277.
- Robinson, A.L., Donahue, N.M., Rogge, W.F., 2006a. Photochemical oxidation and changes in molecular composition of organic aerosol in the regional context. *Journal of Geophysical Research—Atmospheres* 111 (D3), in press. [doi:10.1029/2005JD006265](https://doi.org/10.1029/2005JD006265).
- Robinson, A.L., Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., 2006b. Source apportionment of molecular markers and organic aerosol—1. Polycyclic aromatic hydrocarbons and methodology for data visualization. *Environmental Science and Technology*, in press.
- Robinson, A.L., Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., 2006c. Source apportionment of molecular markers and organic aerosol—2. Biomass smoke. *Environmental Science and Technology*, submitted for publication.
- Robinson, A.L., Subramanian, R., Donahue, N.M., Bernardo-Bricker, A., Rogge, W.F., 2006d. Source apportionment of molecular markers and organic aerosol—3. Food cooking emissions. *Environmental Science and Technology*, submitted for publication.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol .2. noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science and Technology* 27 (4), 636–651.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1997a. Sources of fine organic aerosol .7. Hot asphalt roofing tar pot fumes. *Environmental Science and Technology* 31 (10), 2726–2730.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1997b. Sources of fine organic aerosol .8. Boilers burning No. 2 distillate fuel oil. *Environmental Science and Technology* 31 (10), 2731–2737.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34 (9), 1821–1832.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. *Environmental Science and Technology* 33 (10), 1578–1587.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30 (22), 3837–3855.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002. Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. *Environmental Science and Technology* 36 (6), 1169–1180.
- Simoneit, B.R.T., 1984. Organic-matter of the troposphere .3. Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmospheric Environment* 18 (1), 51–67.

- Simoneit, B.R.T., 1986. Characterization of organic-constituents in aerosols in relation to their origin and transport—a review. *International Journal of Environmental Analytical Chemistry* 23 (3), 207–237.
- Subramanian, R., Khlystov, A.Y., Cabada, J.C., Robinson, A.L., 2004. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. *Aerosol Science and Technology* 38 (S1), 27–48.
- Subramanian, R., Khlystov, A.Y., Robinson, A.L., 2006. Effect of peak inert-mode temperature on elemental carbon measured using thermal-optical analysis. *Aerosol Science and Technology* 40 (10), 763–780.
- Watson, J.G., Fujita, E.M., Chow, J.C., Zielinska, B., 1998a. Northern Front range air quality study final report and supplemental volumes. DRI Document No. 6580-685-8750.1F2. Desert Research Institute, USA, <<http://www.nfraqs.colostate.edu/nfraqs/index2.html>>
- Watson, J.G., Robinson, N.F., Fujita, E.M., Chow, J.C., Pace, T.G., Lewis, C., Coulter, T., 1998b. CMB8 Applications and Validation Protocol for PM_{2.5} and VOCs. US EPA, <http://www.epa.gov/scram001/>
- Wittig, A.E., Anderson, N., Khlystov, A.Y., Pandis, S.N., Davidson, C.I., Robinson, A.L., 2004. Pittsburgh air quality study overview and initial scientific findings. *Atmospheric Environment* 38 (20), 3107–3125.
- Zheng, M., Cass, G.R., Schauer, J.J., Edgerton, E.S., 2002. Source apportionment of PM_{2.5} in the southeastern United States using solvent-extractable organic compounds as tracers. *Environmental Science and Technology* 36 (11), 2361–2371.
- Zielinska, B., Sagebiel, J., McDonald, J.D., Whitney, K., Lawson, D.R., 2004. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *Journal of the Air & Waste Management Association* 54 (9), 1138–1150.